

The Molecular Formula of Cephalosporin P₁

By T. G. HALSALL, E. R. H. JONES, and G. LOWE

(THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY)

THE chemistry of the steroidal antibiotic cephalosporin P₁ has so far been discussed¹ in terms of a molecular formula C₃₂H₄₈O₈ and a parent skeleton of 28 carbon atoms, the molecular weight having been determined by the X-ray crystallographic method. Recently a C₂₉ carbon skeleton has been proposed² for fusidic acid, a similar steroidal antibiotic. The molecular formula of cephalosporin P₁ has now been found to be C₃₃H₅₀O₈, the molecular weight having been kindly determined for us in

the laboratory of Professor C. Djerassi at Stamford University by mass-spectrometric examination of cephalosporin P₁ methyl ester and didiacetylcephalosporin P₁ lactone, using an improved injection technique. The parent skeleton has therefore 29 carbon atoms and an additional methyl group is presumably present, probably at position 8 of the basic steroid ring system. The implications of this closer relationship of cephalosporin P₁ to fusidic acid are being examined.

(Received, December 3rd, 1962.)

¹ Burton, Abraham, and Cardwell, *Biochem. J.*, 1956, **62**, 171; Baird, Halsall, Jones, and Lowe, *Proc. Chem. Soc.*, 1961, 257.

² Godtfredsen and Vangedal, *Tetrahedron*, 1962, **18**, 1029.

A Kinetic Measurement for Fast Cation-Cation Oxidations in Solution

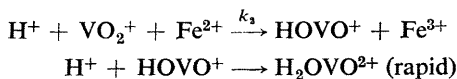
By M. J. NICOL

(UNIVERSITY OF THE WITWATERSRAND, SOUTH AFRICA)

and D. R. ROSSEINSKY

(UNIVERSITY OF EXETER)

THE use of rotating platinum electrodes in polarography, hitherto confined to oxidations involving only one ionic reactant,¹ can be extended to kinetic investigation of fast calomel-cation oxidations provided there exists a suitable applied voltage at which only one species gives a diffusion current. Thus if such an electrode in the system Fe^{II} + V^v $\xrightarrow{k_1}$ Fe^{III} + V^{IV} (in m-perchlorate), is connected by perchlorate solution as a bridge to a standard calomel electrode, and if a potential of 1.0v is applied across the cell, then a diffusion current i_d passes that is proportional only to the iron(II) concentration. Tests for electrode catalysis were negative. From second-order plots based on pen-recorder traces of the diffusion current against time, the rate constant k_1 showed an approximately 1.08th-power dependence on the (excess) hydrogen-ion concentration, indicating the following mechanism:



(Protonation of VO₂⁺ may actually occur in a pre-equilibrium; the non-integral 1.08th order arises from marginal participation of diprotonated VO₃⁺

or from an inconstancy of activity coefficients with medium changes²). The rate constant k_2 is 1.15 × 10⁵ l. mole⁻¹ sec.⁻¹ at 0°, E_a being 3.60 kcal./mole and $\Delta S_{25}^* = -33$ e.u. These values are consistent with the view that predominantly electrostatic effects accompanying the accumulation of charge.

Further reactions apparently amenable to this technique are the interactions Mn^{III}-V^{IV}, Mn^{III}-Fe^{II}, and Co^{III}-Fe^{II}.³ The rate constant of the last reaction does not conform with the Marcus equation,⁴ $k_{ox} = (k'k''K)^{\frac{1}{2}}$, k_{ox} (calc.)⁵ being 5 × 10⁹, and k_{ox} (obs.)³ being 23 l. mole⁻¹ sec.⁻¹. Conformance is expected because of close simulation by such transition-ion oxidations of the corresponding electron-exchange reactions (k' and k''), but it requires also a low equilibrium constant K . More favourable test reactions are V^{III}-Cr^{II} and Co^{III}-Mn^{II}, where k_{ox} (calc.)⁵ are 3 × 10⁻² and 3 × 10³ l. mole⁻¹ sec.⁻¹, respectively.

We thank the South African C.S.I.R. for equipment and a scholarship (to M.J.N.), also the donors for a Leverhulme Commonwealth Fellowship and an I.C.I. Fellowship (to D.R.R.).

(Received, November 23rd, 1962.)

¹ Kolthoff and Reynolds, *Discuss. Faraday Soc.*, 1954, **17**, 167.

² Higginson and Sykes, *J.*, 1962, 2841.

³ Bennett and Sheppard, *J. Phys. Chem.*, 1962, **66**, 1275.

⁴ Marcus, *Discuss. Faraday Soc.*, 1960, **29**, 21.

⁵ Bonner and Hunt, *J. Amer. Chem. Soc.*, 1960, **82**, 3826; table III; Stranks, "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960, p. 163; Latimer, "Oxidation Potentials," Prentice-Hall, New York, 1952.